THE CHEMISTRY OF KAFIR FAT

by

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B. S., Kansas State College
of Agriculture and Applied Science, 1934

A THESIS

submitted in partial fulfillment of the

requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1940

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INTRODUCTION

Any systematic approach to the investigation of new fats necessarily involves a study of the character of the constituents which make up the material. In order to determine these constituents, it is customary to determine the "analytical constants" of the fat, by which is meant those physical and chemical tests which give characteristic values for the different fats, the variation in the constant being only slight for a particular fat if pure. It is plainly evident that these analytical characteristics, while exceedingly useful as criteria of various technical properties, must be supplemented by a more thorough knowledge of the raw materials in order that one may be able to transform these materials into soaps, paints, or other outlets of the fat industry.

Although exhaustive studies have established the constants and compositions of most fats and oils, neither the qualitative nor quantitative chemical composition of fat from kafir grain has been definitely established. Francis and Friedemann (3) reported a few of the constants and gave an approximate analysis. In view of the fact that much information is lacking with regard to the chemical composition, it was thought well worth while to investigate this

problem again.

EXPERIMENTAL DATA

Extraction and Purification

Quite a number of solvents have been proposed for the commercial extraction of fats. Of these, Skelly Solve B, ether, benzene, carbondisulfide, toluene, chloroform, ethylene dichloride, ethyl alcohol, carbon tetrachloride, and acetone were used in the experimental run to determine which would give the best fat extraction. It was found that Skelly Solve B, ether, benzene, and carbon disulfide all gave a product which had characteristics of a good fat sample. Each extraction gave a fat percent of 3.5 to 4.0. Of these, Skelly Solve B, despite the high inflammability, was selected because it is cheap, relatively inert, fairly easily removed from both fat and meal and because it extracts a maximum amount of fatty-matter.

About 33 pounds of Blackhull kafir grain were placed in the Pfaudler (soxhlet) extractor and allowed to run for 24 hours. It was found that this length of time completed the extraction.[1] The extracted sample was decolorized and freed of solid particles by the addition of adsorbents. The

[1] Olsen, A. L. Unpublished data.

residual solvent was removed under diminished pressure, using a capillary tube attached to a source of nitrogen.

The extraction, purification, slipping points, and the percent volatile were carried out with the aid of NYA students.

Determination of Physical Constants

Melting Point. Modification of Wiley Method. The melting point is the temperature at which the fat becomes liquid. The following method for the determination of this constant has been proposed (4). A heavy brass plate, fitted on a chilling bath, was drilled with holes 9.5 mm. in diameter and 3.2 mm. deep. The melted fat was poured into these holes and allowed to cool for two or three hours. An alcohol-water mixture was made by carefully pouring a quantity of 95 percent ethyl alcohol down the side of the tube containing the water. Two layers were formed, the intersection of which brought about a specific gravity equal to that of the fat. The tube, 30 X 3.5 cm., containing the alcohol-water mixture, was cooled in an ice bath and the disk of fat dropped into it. As the surrounding water bath was heated, the alcohol-water mixture was gently stirred, with a thermometer just above the disk. The heat was so regulated that about 10 minutes were required for the last 2 degrees

increase in temperature. As soon as the fat mass became spherical, the thermometer was read and the temperature was recorded.

Slipping Point Method. The following method for the determination of this constant has been described (5). The fat was drawn into thin-walled capillary tubes 1 mm. in diameter and allowed to cool in an ice box for 12 to 15 hours. Then the tube was attached to the bulb of a thermometer, immersed in a large beaker of water, and heated slowly. The temperature at which the fat rose in the tube was taken as the melting point.

Titer. The titer is the temperature at which the fatty acids become solid. The following method for the determination of this constant has been adopted (1). Seventy-five cc. of glycerol KOH solution were heated to 150° C. and 50 cc. of the melted fat were added. The temperature was kept at about 150° C. for 15 minutes to complete the saponification. The soap solution was poured into 500 cc. of hot water and 50 cc. of 25 percent H_2SO_4 were added. The solution was then heated, with frequent stirring, until the layer of fatty acids separated out perfectly clear. The fatty acids were washed free of all mineral acids, filtered, dried, and poured into the titer tube.

The titer tube was placed in a water bath of about 20° C. and stirred slowly until the temperature remained constant for 30 seconds. The thermometer was then allowed to hang quietly, with the bulb in the center of the mass, and the highest temperature to which the mercury column rose was taken as the titer of the fatty acids.

Specific Gravity. The specific gravity is the weight per unit volume. The method for the determination of this constant is that of Bailey, et al (1). The specific gravity was determined by means of a pycnometer at a temperature of 65° C.

Refractive Index. The refractive index is the degree of deflection caused in a ray of light in passing from one transparent medium into another. For the determination of this constant, the method of Bailey, et al (1) was used. The index of refraction was determined by direct readings of the Abbe Refractometer at a temperature of 65° C.

Percent of Volatile Matter. The percent of volatile matter is the percent of water and volatile matter lost when heated at 110° C. for 30 minutes. The method for the determination of this constant has been described by Jamieson (5). Ten grams of the fat were weighed into a weighing

dish and placed in an oven at 110° C. for 30 minutes. A current of inert gas was passed through the oven to prevent oxidation. The loss of weight was then determined.

Calculations.

$$\text{Percent volatile} = \frac{a}{w}$$

a = loss of weight of sample

w = weight of sample

Determination of Chemical Constants

Iodine Number. The iodine number gives the number of grams of iodine absorbed by 100 grams fat, and is a measure of the unsaturation present. The method for the determination of this constant was that of Bailey, et al (1). One-tenth to five-tenths gram of fat was dissolved with 15 cc. of CCl_4 in a 250 cc. glass-stoppered bottle. Twenty-five cc. of the Wijs reagent were added, by means of a pipette, and the mixture was then placed in the dark for 30 minutes. At the end of this time 15 cc. of a 15 percent solution of KI and 100 cc. of distilled water were added. The excess halogen was titrated with 0.10 N $Na_2S_2O_3$ solution. Starch was used as an indicator. The Wijs reagent was standardized under identical conditions in a blank test.

Calculations.

$$\text{Iodine number} = \frac{a - b}{w} \times 1.269$$

a = cc. of 0.10 N $Na_2S_2O_3$ used for blank titration

b = cc. of 0.10 N $Na_2S_2O_3$ used for fat sample

w = weight of fat sample

Acid Number. The acid number is the number of milligrams of KOH needed to neutralize the free fatty acid in 1 gm. of fat. For the determination of this constant the method of Bailey, et al (1) was adopted. Five grams of fat were weighed out in a flask and 75 cc. of 95 percent neutral alcohol were added. The fat was dissolved by warming and gentle shaking, then titrated with 0.10 N KOH. Phenolpthalein was used as an indicator.

Calculations.

$$\text{Acid number} = \frac{5.611 \times a}{w}$$

a = titration

w = weight of fat sample

Oleic acid = a X 0.0282 g.

Saponification Number. The saponification number is the number of milligrams of KOH required to saponify 1 gm. of fat. The following method for the determination of this

constant has been described by Jamieson (5). Five grams of fat were saponified with exactly 25 cc. of alcoholic KOH, by heating under a reflux for one hour. The excess KOH was titrated with 0.5 N HCl, using Thymol Blue as an indicator. Two blank determinations were run at the same time.

Calculations.

$$\text{Saponification number} = \frac{5.611\ (b - a)}{w}$$

a = titration of sample

b = titration of blank

w = weight of sample

Ester value = a - b

a = saponification value

b = acid value

Percent glycerin = 0.0547 X ester value

Soluble Acids. The soluble acids are those fatty acids which are soluble in hot water. To determine this constant, the method of Bailey, et al (1) was adopted. The flask used for saponification and its contents were placed on a steam bath and the alcohol evaporated. The contents then were made acid, by adding 1 cc. of 0.5 N HCl in excess and heated on the steam bath until the fatty acids formed a clear layer on the upper surface. In three successive treatments, the flask was filled to the neck with hot water

and then cooled in ice water until the cake of fatty acids was hardened. Each time the liquid was filtered into a liter flask. The combined washings were titrated with 0.10 N KOH, using phenolphthalein as an indicator.

Calculations.

Weight of soluble acids = (a - 5) 0.0088

a = titration

5 = excess of 1 cc. of 0.5 N HCl

0.0088 = milligrams of butyric acid

Percent soluble acids = $\frac{b}{w}$

b = weight of soluble acids

w = weight of fat sample

Insoluble Acids. The insoluble acids are those fatty acids which are not soluble in water. The method of Bailey, et al (1) was used for this determination. The flask containing the insoluble acids from the saponification and soluble acid determination was allowed to drain for 12 hours. The cake was then placed in a weighed flask with the aid of hot absolute alcohol, the alcohol evaporated, and the sample dried for two hours in an oven at 100°C. After cooling in a desiccator, the sample was weighed.

Calculations.

$$\text{Percent insoluble acids} = \frac{a}{w}$$

a = weight of insoluble acids

w = weight of fat sample

Percent Unsaponifiable Matter. The percent unsaponifiable matter is the substances which are not saponified by alkali but are soluble in ether. The method for the determination of this constant has been described by Jamieson (5). Five grams of fat were saponified with 25 cc. of alcoholic KOH by refluxing for one hour. The solution was then poured into a 500 cc. separatory funnel with the aid of three successive 50 cc. portions of ether.

The ether extracts were washed by gently rotating until the wash water no longer turned phenolphthalein red. The ether solution was then vigorously shaken with distilled water, the layers separated, and the ether solution filtered into a weighed flask. The ether was evaporated and the unsaponifiable dried in an oven at 105° C.

Calculations.

$$\text{Percent unsaponifiable} = \frac{a}{w}$$

a = weight of unsaponifiable

w = weight of fat sample

Acetyl Value. The acetyl value is the number of milligrams of KOH required to neutralize the acetic acid set free by hydrolysis of one gram of acetylated fat. The method of Bailey, et al (1) was used for the determination of this constant. Ten grams of fat were refluxed for two hours with twice this amount of acetic anhydride in a 500 cc. round-bottom flask. The mixture was then boiled with 500 cc. of water for 15 minutes while bubbling a stream of air through the solution to prevent bumping. The water was siphoned off and the sample was washed two more times with 500 cc. of water. The neutral acetylated fat was allowed to stand for one hour with five grams of anhydrous Na_2So_4, filtered, and dried in an oven at 100° C. The saponification number of both acetylated and original fats was determined.

Calculations.

$$\text{Acetyl value} = \frac{S_2 - S_1}{(1 - 0.00075)S_1}$$

S_1 = saponification number of original fat

S_2 = saponification number of acetylated fat

Thiocyanogen Number. By means of this method, the percentages of oleic, linoleic, linolenic, and saturated acids in an oil may be determined, provided other unsaturated acids are not present. For the determination of this

constant, the method of Irwin, et al (4) was used. For the preparation of one liter of 0.2 N solution of thiocyanogen, 50 grams of dry lead thiocyanate were suspended in 500 cc. of anhydrous acetic acid, and 16.2 grams of bromine were dissolved in another 500 cc. of acid. The bromine solution was slowly added to the lead thiocyanate suspension in small portions and shaken vigorously between each addition until the solution was completely decolorized. After all the bromine had been added, the solution was filtered as quickly as possible.

One-tenth to three-tenths gram of fat was weighed into a dry 125 cc. glass-stoppered flask. Twenty-five cc. of the thiocyanogen solution were added and the sample allowed to stand for 24 hours in the dark at 18° to 21° C. At the end of the 24-hour period, 1 gram of dry powdered KI was added and the flask was swirled rapidly for two minutes. Thirty cc. of distilled water were added and the liberated iodine was titrated with 0.1 N $Na_2S_2O_3$, using starch as an indicator. Three blanks were run with the samples.

Calculations.

$$T.V. = \frac{(a - b)\ N_2S_2O_3 \text{ factor} \times 100}{w}$$

a = blank titration
b = sample titration
w = weight of sample

$Na_2S_2O_3$ is expressed as grams of I_2 per cc.

The following calculations were used to express the percentages of the various acids as glycerides.

L.G. = 1.154 (I.V. - T.V.)

O.G. = 1.162 (2 T.V. - I.V.)

S.G. = 100% - (L.G. + O.G.)

I.V. = iodine number of fat

T.V. = thiocyanogen number of fat

S.G. = percent of saturated glycerides

O.G. = percent of oleic glycerides

L.G. = percent of linoleic glycerides

The following calculations were used when the iodine number and thiocyanogen number were determined directly on the fatty acids.

% L.A. = 1.104 (I.V. - T.V.)

% O.A. = 1.112 (2 T.V. - I.V.)

% S.A. = 100% - %(L.A. + O.A.)

Reichert-Meissl Number. The Reichert-Meissl number is the number of cc. of 0.1 N NaOH used to titrate the soluble volatile acids in five grams of fat. The method of Bailey, et al (1) was used. Five grams of fat were saponified with 20 cc. of glycerin sodium hydroxide solution. When the solution cooled, 135 cc. of water were added to dissolve the soap. Then 6 cc. of 20 percent H_2SO_4 solution and a few

pieces of pumice were added. The flask was heated at such a rate that 110 cc. were distilled in about 30 minutes. After the flask, containing the distillate, had been immersed in water at 15° C. for 15 minutes, the insoluble acids were filtered and 100 cc. of the filtrate were titrated with 0.1 N NaOH, using phenalphthalein as an indicator.

Calculations.

(1) $a \times \frac{11}{10} = b$

a = titration of 100 cc.

b = titration of 110 cc.

(2) a:b::5:x

a = weight of sample

b = titration of 110 cc.

x = Reichert-Meissl number

Polenske Number. The Polenske number is the number of cc. of 0.1 N NaOH used to titrate the insoluble volatile acids in five grams of fat. Bailey, et al (1) proposed the following method for the determination of this constant. The remainder of the soluble acids was removed from the insoluble acids upon the filter paper by three successive 15 cc. portions of water, previously passed through the condenser, graduate cylinder, and 100 cc. flask. The insoluble acids were then dissolved by passing successive 15 cc.

portions of neutral alcohol through the filter, each portion having previously passed through the condenser, graduate cylinder, and 110 cc. flask. The combined alcoholic washings were titrated with 0.1 N NaOH, using phenolphthalein as an indicator.

Calculations.

The Polenske number equals the number of cc. of 0.1 N NaOH used for titration.

Separation of Liquid and Solid Fatty Acids. Modified Twitchell Method. The following method has been proposed by Irwin, et al (4). A sample of pure fatty acid, which would give about one and two-tenths grams of solid fatty acids, was weighed into a 250 cc. beaker. One and five-tenths grams of powdered lead acetate were weighed into another beaker and 50 cc. of absolute alcohol were added to each. After both had been boiled, the lead acetate was added to the alcoholic fatty acids. The sample was then cooled and placed in an ice bath at 15° C. for two hours. After the lead soaps had been filtered and washed with 200 cc. of cold alcohol, they were transferred into the original beaker with 100 cc. of absolute alcohol and made 0.5 percent acetic acid. The lead soaps were then brought to a boil, cooled to room temperature, and placed in an ice box overnight.

The next day the sample was filtered and washed as before. Then, by the aid of ether, the soaps were taken to the original beaker and broken up by adding 20 cc. of 25 percent nitric acid. The ether solution was washed free of acid, transferred to a weighed flask, and evaporated under a current of inert gas. The sample was dried in an oven at 103° C. for one hour, cooled, and the weight was taken.

Calculations.

$$\frac{\text{Weight of solid acids}}{\text{Weight of sample}} \times 100 = \text{percent of solid fatty acids}$$

The percentage of component acids was calculated according to the following formulas:

I.N. = iodine number of solid acids

T.N. = thiocyanogen number of solid acids

C = percent of solid acids uncorrected

D = percent of liquid acids uncorrected

E = percent of unsaturated acids by thiocyanogen method

L.A. in solid acids = 1.104 (I.N. - T.N.) X C

O.A. in solid acids = 1.112 (2 T.N. - I.N.) X C

Solid saturated acids = C - (L.A. + O.A.)

Saturated acids in liquid acids = D + (L.A. + O.A.) - E

Total saturated acids = percent of solid acids (as found) - (oleic in solid acid + linoleic in solid acid) + saturated acids in liquid acids

Total unsaturated acid = 100 - total saturated acids

Total oleic acid =

$$\frac{(\text{unsaturated acids} \times 181) - (\text{I.V.M.F.A.} \times 100)}{91}$$

Total linoleic acid =

total unsaturated acids - total oleic acid

Separation of Saturated and Unsaturated Fatty Acids. Lead Salt-Ether Method. The method for the determination of this constant was that of Bailey, et al (1). Ten grams of fat were saponified and made slightly acid with acetic acid. KOH was added until the solution gave a distinct pink with phenolphthalein. The soap solution was boiled five minutes with 20 percent lead acetate, shaken thoroughly, and cooled under running water. The liquid was poured off and the lead soaps refluxed with 120 cc. of ether until completely dissolved. Enough ether was added to bring the total volume to 150 cc. and then the sample was placed in an ice box overnight. After remaining overnight, the lead soaps were filtered and washed several times with small portions of ether, and then transferred to a separatory funnel with 50 cc. of ether. After the lead soaps had been completely disintegrated by shaking, they were allowed to stand for 20 minutes and 20 cc. of 50 percent HCl solution was added.

When the two layers had separated, the aqueous layer was drawn off and the ether solution washed free of acid. The sample was dehydrated with two grams of Na_2SO_4 and transferred to a weighed flask. The ether was distilled and the sample dried in an oven at 110° C.

The ether solution of soluble lead soaps was transferred to a separating funnel and completely shaken with a mixture of 30 cc. of HCl and 75 cc. of water. After standing 10 minutes, the aqueous layer was drawn off and the ether solution washed free of acid. The ether was evaporated from a weighed flask, through which passed a current of inert gas. The sample was then dried in an oven, containing inert gas, at a temperature of 110° C.

The iodine numbers of both the saturated and unsaturated portions were obtained by the regular Wijs method.

Calculations.

$$\text{Saturated acids} = \frac{a}{w}$$

a = weight of saturated acids

w = weight of fat sample

$$\text{Unsaturated acids} = \frac{a}{w}$$

a = weight of unsaturated acids

w = weight of fat sample

To correct for the unsaturated acids in the fraction of saturated acids, the following formula was used.

$$\frac{\text{Iod. No. of saturated acid X 100}}{\text{Iod. No. of unsaturated acid}} = A$$

$$\frac{A \times B}{100} = \text{correction}$$

A = percentage of unsaturated acids in saturated acid fraction

B = saturated acids as found by analysis

The correction was subtracted from the saturated fraction and added to the unsaturated fraction.

The physical and chemical constants are recorded in Tables 1 and 2.

INTERPRETATION OF RESULTS

In order that a representative value for the physical and chemical constants could be recorded, determinations were made on 14 different fat samples, extracted as nearly as possible under the same conditions. One sample, number IX, was divided into two parts. One part was purified and the other was taken as it came from the extractor with only the solvent being removed. This was done to determine if any of the fat materials were being removed during the prodess of purification. The results show that the constants of the two fractions parallel very closely, proving the method of purification to be satisfactory. The following

Table 1. Physical constants.

Sample	Melting point: Wiley modification	Melting point: Slipping point*	Titer	Specific gravity at 65° C.	Refractive index at 65° C.	Per cent volatile*
I						0.49
II						0.48
III						0.17
IV						
V		57.0 57.0 57.2				1.25
VI		62.8 62.4 62.8		0.8796	1.4562 1.4560	0.81
VII		63.5 63.3 63.5				0.51
VIII		62.8 63.0 62.5			1.4574 1.4571	2.87
IX A		65.0 65.2 64.0			1.4572 1.4571	0.79
IX B	61.2 61.5	60.0 60.0 60.0			1.4566 1.4569	1.11
X		61.0 61.0 60.8				1.71
XI		64.0 64.2 63.8			1.4542 1.4544	2.88

* These constants were determined by Rex Toomey and Oscar Brumback, N.Y.A. students.

Table 1. (Continued)

Sample	Melting point		Titer	Specific gravity at 65° C.	Refractive index at 65° C.	Per cent volatile
	Wiley modification	Slipping point				
XII	63.6 63.2	62.0 62.2 62.6		0.8773	1.4554 1.4555	2.68
XIII	62.0 61.3	59.8 59.4 60.0	43.5 43.7 43.6		1.4572 1.4576	1.74
XIV	62.5 63.3	61.8 62.2 61.2	43.5 43.7 44.0			2.50
XV		64.0 64.2 64.4				0.89
Fatty acids					1.4512 1.4509	

Table 2. Chemical constants.

Sample	Iodine number	Acid number	Saponification number	Soluble acids	Insoluble acids	Per cent unsaponifiable matter	Acetyl value	Thiocyanogen number	Reichert-Meissl number	Polenske number	Saturated acids	Unsaturated acids
I		8.48	181.9			5.2						
		8.51	182.1			5.1						
		8.49	181.1									
II		8.04	171.5									
		8.26	171.5									
		8.25	171.2									
III		16.18	164.6			5.95						
		16.5	175.2			5.91						
		17.0										
IV		7.48	166.7			4.91			.67	.23		
		7.51	166.5			4.98			.66	.24		
		7.59										
V		13.69	186.3			5.05			.74	.27		
		13.75	186.8			5.10			.68	.22		
		13.73	186.9									
VI	106.6	14.6	179.2			5.65	14.2					
	106.5	15.2	171.4			5.78	14.0					
	106.8	15.6	175.1									
VII	109.6	7.88	189.7			5.55						
	110.1	7.87	193.1			5.29						
	110.6	7.84	192.1									
VIII	111.7	8.98	180.8									
	112.1	9.12	180.8									
	112.6	9.02										

Table 2. (Continued)

Sample	Iodine number	Acid number	Saponification number	Soluble acids	Insoluble acids	Per cent unsaponifiable matter	Acetyl value	Thiocyanogen number	Reichert-Meissl number	Polenske number	Saturated acids	Unsaturated acids
IX A	111.5	10.5	175.5									
	111.4	10.4	174.9									
	111.4	10.5										
IX B	111.1	10.8	174.9				15.6		.58	.23		
	111.4	10.5	174.6				14.6					
	111.7	10.4	---									
X	109.1	13.29							.68	.21		
	108.8	13.37							.63	.22		
	108.9	13.24										
XI	105.8	9.41										
	106.3	9.41										
	106.1	9.42										
XII	104.7	9.04	164.7	.68	90.6		21.8					
	105.2	8.99	165.0	.85			19.2					
	104.7	9.03	162.6									
XIII	109.2	11.4	176.6	.33	90.7			70.2	.51	.26		
	109.5	11.5	177.2	.55	91.7			72.8	.67	.20		
	109.5	10.8		.56	92.4			71.6				
XIV	105.6	11.5	163.6	.68	92.7		20.4				12.17	74.03
	105.5	11.6	163.9	1.09	91.9		20.2				11.71	77.09
		11.5	167.0		92.8							
XV		6.2										
		6.14										
		6.2										
Fatty acid	113.7							73.1			19.8	80.2
	113.7							72.8			19.8	80.2
	113.4							74.2			19.98	80.02

constants represent a typical value of many determinations made upon these extractions:

Melting point, 62° C.; titer, 43.5° C.; specific gravity at 65° C., 0.8796; refractive index at 65° C., 1.4562; percent volatile, 0.89; iodine number, 110; acid number, 10.4; saponification number, 171.2; soluble acids, 0.68 percent; insoluble acids, 92.8 percent; unsaponifiable, 5.95 percent; acetyl value, 14.6; thiocyanogen number, 71.9; Reichert-Meissl number, 0.67; Polenske number, 0.23; saturated acids, 19.8 percent; unsaturated acids, 80.2 percent; oleic acid, 36 percent; linoleic acid, 44 percent.

The purified fat has a white color, fatty taste, a fatty odor, and a consistency of grease, each being a characteristic of vegetable fats and oils. The physical characteristics given in Table 1 were determined for the purpose of ascertaining the general properties of the fat. These physical characters do not vary greatly for any given kind of fat, provided it is examined under the same conditions. The specific gravity and refractive index, for instance, fall in the range of other fats. Since the fats are mixtures of various glycerides, they do not show a sharp melting point characteristic of pure organic compounds. Because of this, it is very difficult to get the melting

points to check. However, the melting point of kafir fat, by the slipping point method, checked very well with the modified Wiley method. In each case the Wiley method gave results about 1° C. higher than the slipping point. The melting point ran high in comparison with other similar vegetable fats. This is probably due to the high percent of unsaponifiable. During the process of purification, much trouble was met in removing the solvent. It was found, by bubbling a current of inert gas through the mixture, that the solvent was readily removed by heating under diminished pressure. The low percent volatile indicates that all the Skelly Solve B had been removed. It also indicates that the percentages of moisture and volatile acids are very low.

The chemical constants in Table 2 were determined for the purpose of ascertaining the general composition of the fat, as well as to furnish a basis for comparison with other vegetable fats and oils.

Kafir fat, with an iodine number of 110, belongs to the semi-drying class. Iodine itself is absorbed very slowly by the fat; hence the reaction is usually carried out in such a manner that the addition will take place through the agency of iodine chloride or bromide (6).

The presence of a fairly high acid number indicates that some decomposition of the glycerides has taken place. This is usually caused by chemical treatment or bacterial action, accelerated by light and heat. The free fatty acid may be expressed as the percent of free oleic acid (5).

The saponification number is inversely proportional to the mean molecular weights of the fatty acids present, its principal value being to indicate the presence of the lower fatty acids (6). Kafir fat with a saponification number of 170 indicates that some of the lower molecular weight fatty acids are present.

Only 0.68 percent soluble acids was found to be present. This probably is butyric acid. The percentage of insoluble acids, 92 percent, has not been corrected for the presence of unsaponifiable. Since the percent of unsaponifiable is about 5, the actual percent of insoluble acids is about 87.

It is very common for vegetable fats and oils to contain about 1 percent unsaponifiable. However, this is not true of kafir fat, for its value was determined to be about 5 percent. The difficulties encountered in establishing many of the constants may be traced to the high percent of unsaponifiables.

The acetyl value, 14 to 20, indicates a small amount of glyceride of hydroxylated acids. This value is also affected by the free alcohols, as phytosterol or cholesteral, as well. If the acetyl value of a fat is high, as in the case of castor oil (2), one can dehydrate the hydroxylated acids, bringing about a greater degree of unsaturation.

The thiocyanogen number, in conjunction with the iodine number, enables one to calculate the percent of oleic, linoleic, and saturated acids. The same is true of the glycerides. In each case it is assumed that no unsaturation greater than linoleic is present. In cases where the unsaponifiable is high, the thiocyanogen numbers are very hard to determine (5). In this case it is advisable to make the determinations directly upon the free fatty acids. The percentage of glycerides and free fatty acids were as follows:

L.G., 43.28%	O.G., 39.9%	S.G., 16.75%
L.A., 44.38%	O.A., 36.69%	S.A., 18.93%

The low Reichert-Meissl and Polenske numbers indicate the almost complete absence of glycerides of volatile acids. Most volatile acids of fats and oils consist chiefly of those in series from butyric to lauric acids (5).

The saturated and unsaturated fatty acids were separated in two ways. The modified Twitchell method (4) involves the conversion of the acids to their lead salts,

which, in case of the saturated acids, are insoluble, while those of the unsaturated acids are soluble in cold alcohol. By taking the iodine and thiocyanogen numbers of the saturated fraction, it was possible to determine the percent of oleic, linoleic, and saturated fatty acids. The results were as follows: L.A., 45.82 percent; O.A., 34.2 percent; S.A., 19.98 percent. The lead salt-ether method involves the conversion of the acids to their lead salts, which, in case of the saturated acids, are insoluble, while those of the saturated are soluble in cold ethyl ether. Due to the solubility of the salts of the saturated acids as well as the insolubility of the salts of the unsaturated acids, it is almost impossible to effect a complete separation by this procedure (5). The saturated fraction absorbed some iodine, showing the presence of unsaturated acids. The unsaturated fraction was contaminated with small amounts of the saturated acids, but this error was much smaller than the first. A correction for this contamination was made and the following results were obtained: saturated acids, 12.17 percent; unsaturated, 74.03 percent. These values are not corrected for the presence of the unsaponifiable matter.

The following shows a comparison of those constants already determined and those established in this laboratory:

	Constants previously established (1)	Constants established in this laboratory
Specific gravity	0.9398 at 15° C.	0.8796 at 65° C.
Melting point	44.2° C.	62° C.
Saponification number	193.6	171.2
Iodine number	109.7	110
Reichert-Meissl number	4.3	0.67
Insoluble acids	93.2%	92.8%
Acetyl value	42.3	14.6
Titer	34° C.	43.5° C.
Unsaponifiable	1.72%	5.95%
Soluble acids	0.66%	0.68%
Liquid acids	85.98%	80.2%
Solid acids	7.48%	19.8%
Free fatty acid	27.02	10.4

The constants which have been previously established were made upon kafir fat that was extracted by ether. Those constants which were established in this laboratory were made upon kafir fat that was extracted by Skelly Solve B.

CONCLUSION

1. A number of solvents have been investigated for the extraction of fats from kafir grain. Skelly Solve B was found to be the most efficient.

2. The physical and chemical constants have been determined on a number of fat extractions from Blackhull kafir grain. These constants have been used to establish the presence of certain constituents.

3. These values have been compared with the data which have been recorded.

ACKNOWLEDGMENT

Appreciation is expressed to Dr. A. L. Olsen, Instructor in Chemistry for helpful suggestions in research and in the planning of the thesis; and to Rex Toomey and Oscar Brumback, NYA students, for assistance in the extraction and purification of the kafir fat.

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